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=> imidazole
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=> s imidazole
         40909 IMIDAZOLE
          7362 IMIDAZOLES
L1       43094 IMIDAZOLE
                (IMIDAZOLE OR IMIDAZOLES)

=> s l1 and sodium
        753630 SODIUM
            31 SODIUMS
        753643 SODIUM
                (SODIUM OR SODIUMS)
L2        2278 L1 AND SODIUM

=> s l2 and pKa
         27063 PKA
           397 PKAS
         27246 PKA
                (PKA OR PKAS)
L3          33 L2 AND PKA

=> s imidazolate
           504 IMIDAZOLATE
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            28 IMIDAZOLATES
L4         511 IMIDAZOLATE
                (IMIDAZOLATE OR IMIDAZOLATES)

=> s l4 and pKa
         27063 PKA
           397 PKAS
         27246 PKA
                (PKA OR PKAS)
L5          27 L4 AND PKA

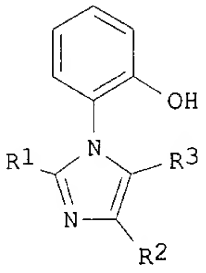
=> dis l5 1-27 bib abs

L5   ANSWER 1 OF 27  CAPLUS  COPYRIGHT 2002 ACS
AN   2002:90113  CAPLUS
DN   136:153008
TI   Heparin-derived polysaccharide mixtures, preparation method and
     pharmaceutical compositions containing same
IN   Diaz, Jacques; Pecquet, Christelle; Perrin, Elisabeth; Viskov, Christian
PA   Aventis Pharma S.A., Fr.
SO   PCT Int. Appl., 30 pp.
     CODEN: PIXXD2
DT   Patent
LA   French
FAN.CNT 1
     PATENT NO.        KIND  DATE           APPLICATION NO.  DATE
     ---------------   ----  --------       ---------------  --------
PI   WO 2002008295     A1    20020131       WO 2001-FR2332   20010718
         W:  AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN,
             CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
             GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
             LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT,
             RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ,
             VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
         RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY,
             DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF,
             BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
     FR 2811992         A1    20020125       FR 2000-9572     20000721
     US 2002055621      A1    20020509       US 2001-909797   20010723
PRAI FR 2000-9572       A     20000721
     US 2000-229123P    P     20000831
OS   MARPAT 136:153008
AB   The invention concerns heparin-derived polysaccharide mixts. having mol.
     wt. 1500-3000, anti-Xa activity 100-150 UI/mg, anti IIa activity 0-10
     UI/mg, anti-Xa activity/anti-IIa activity >10, 2-26 saccharide groups,
     4,5-glucuronic 2-O-sulfate terminal groups, under alkali or alk.-earth
     metal salt form.  These mixts. are manufd. by depolymn. of quaternary
     ammonium salts of benzyl esters of heparin in org. solvent using a strong
     org. base having pKa >20 or Na imidazolate,
     transforming the resulting quaternary ammonium salt of the depolymd.
     benzylic ester to the Na salt, and sapon. of the ester.
RE.CNT  4     THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD
              ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5   ANSWER 2 OF 27  CAPLUS  COPYRIGHT 2002 ACS
AN   2000:701394  CAPLUS
DN   134:67668
TI   4-Nitroimidazole Binding to Horse Metmyoglobin: Evidence for Preferential
     Anion Binding
AU   Taylor, Kevin C.; Vitello, Lidia B.; Erman, James E.
CS   Department of Chemistry and Biochemistry, Northern Illinois University,
     DeKalb, IL, 60115, USA
SO   Archives of Biochemistry and Biophysics (2000), 382(2), 284-295
     CODEN: ABBIA4; ISSN: 0003-9861
```

PB Academic Press
DT Journal
LA English
AB The ionization of 4-nitroimidazole to 4-nitroimidazolate was investigated as a function of ionic strength. The apparent **pKa** varies from 8.99 to 9.50 between 0.001 and 1.0 M ionic strength, resp., at 25.degree.C. The ionic strength dependence of this ionization is anomalous. The binding of 4-nitroimidazole by horse metmyoglobin was studied between pH 5.0 and 11.5 and as a function of ionic strength between 0.01 and 1.0 M. The assocn. rate const. is pH-dependent, varying from 24 M-1s-1 at pH 5 to a max. value of 280 M-1s-1 at pH 9.5 and then decreasing to 10 M-1 s-1 at pH 11.5 in 0.1 M ionic strength buffers. The dissocn. rate const. has a much smaller pH dependence, varying from 0.082 s-1 at low pH to 0.035 s-1 at high pH, with an apparent **pKa** of 6.5. The binding affinity of 4-nitroimidazole to horse metmyoglobin is about 2.5 orders of magnitude stronger than that for imidazole and this increased affinity is attributed to the much slower dissocn. rate for 4-nitroimidazole compared to that of imidazole. Although the ionic strength dependence of the binding rate is small and secondary kinetic salt effects can account for the ionic strength dependence of the assocn. rate const., the pH dependence of the rate consts. and microscopic reversibility arguments indicate that the anionic form of the ligand binds more rapidly to all forms of metmyoglobin than does the neutral form of the ligand. However, the spectrum of the complex is similar to model complexes involving neutral imidazole and not **imidazolate**. The latter observation suggests that the initial metmyoglobin/4-nitroimidazolate complex rapidly binds a proton and the neutral form of the bound ligand is stabilized, probably through hydrogen bonding with the distal histidine.
RE.CNT 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 3 OF 27 CAPLUS
AN 2000:229216 CAPLUS
DN 133:89476
TI Syntheses and **pKa** determination of 1-(o-hydroxyphenyl)imidazole carboxylic esters
AU Collman, James P.; Wang, Zhong; Zhong, Min; Zeng, Li
CS Department of Chemistry, Stanford University, Stanford, CA, 94305-5080, USA
SO Perkin 1 (2000), (8), 1217-1222
CODEN: PERKF9
PB Royal Society of Chemistry
DT Journal
LA English
GI



I

AB All three isomers of 1-(o-hydroxyphenyl)imidazole carboxylic esters I (R1

= CO2Me, R2 = R3 = H; R1 = R3 = H, R2 = CO2Me; R1 = R3 = H, R3 = CO2Et) have been synthesized regioselectively via their Me ether precursors. Me 1-(o-methoxyphenyl)imidazole-2-carboxylate and the corresponding 1,4-isomer were synthesized via Cu-catalyzed coupling of 2-iodoanisole with imidazole followed by methoxycarbonylation, and by direct coupling of 2-iodoanisole with Me imidazole-4-carboxylate, resp. The 1,5-isomer was prepd. by annulation of an N-aryl glycine ester deriv. The boron tribromide mediated cleavage of Me ethers gave the hydroxyphenyl compds. I in good to excellent yields. These compds. can serve as building blocks for synthesizing a new generation of active-site model compds. of cytochrome c oxidase (CcO). The **pKa** values have been detd. by spectrophotometric measurements in order to provide a basis for the understanding of the proton transfer processes in CcO.

RE.CNT 35 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 4 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 2000:136030 CAPLUS
DN 132:276146
TI Metal-Bound Histidine Modes in UV Resonance Raman Spectra of Cu, Zn Superoxide Dismutase
AU Wang, Daojing; Zhao, Xiaojie; Vargek, Maria; Spiro, Thomas G.
CS Department of Chemistry, Princeton University, Princeton, NJ, 08544, USA
SO Journal of the American Chemical Society (2000), 122(10), 2193-2199
CODEN: JACSAT; ISSN: 0002-7863
PB American Chemical Society
DT Journal
LA English
AB UV resonance Raman [UVRR] spectra of Cu, Zn superoxide dismutase [SOD] contain bands arising from vibrations of metal-bound histidine ligands. Spectra in H2O soln. reveal several modes of the His61 side chain, which bridges the Cu2+ and Zn2+ ions as **imidazolate**. The disappearance of these bands signals disruption of the bridge when the pH is lowered to 3.0, or the Cu2+ is reduced to Cu+. Binding of hydroxide [pH 12] or cyanide to the Cu2+ perturbs the **imidazolate** modes, reflecting geometry changes induced by these strong-field ligands. In D2O soln. several addnl. bands become enhanced which arise from histidine ligands that have undergone NH/D exchange. Some of these are attributed to Cu-bound ligands and others to Zn-bound ligands, on the basis of selective changes accompanying removal and replacement of the metals. Excitation profiles are similar for these bands, and for the bridging **imidazolate** bands; they are red-shifted relative to nonligating histidine. The detection of site-specific histidine ligand modes gives promise for wide applicability of UVRR spectroscopy in studying histidine ligation in metalloproteins. The single tyrosine residue of SOD, which is a target of active-site-catalyzed nitration by peroxynitrite, is found to have an elevated **pKa**, 11.4, despite being exposed to solvent.

RE.CNT 46 THERE ARE 46 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 5 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1999:541847 CAPLUS
TI Interesting electrochemical behavior of copper-zinc superoxide dismutase on mercury electrode.
AU Luo, Qin-Hui; Shen, Meng-Chang; Wang, Zhi-Lin; Qian, Wen
CS Coordination Chemistry Institute, Nanjing University, Nanjing, 210093, Peop. Rep. China
SO Book of Abstracts, 218th ACS National Meeting, New Orleans, Aug. 22-26 (1999), INOR-395 Publisher: American Chemical Society, Washington, D. C.
CODEN: 67ZJA5
DT Conference; Meeting Abstract
LA English
AB The electrochem. behaviors of CuZn-SOD on mercury electrode were studied by cyclic voltammetry and direct polarog. The results showed that SOD was

absorbed rapidly on the surface of electrode, and the redox process was controlled by diffusion. In the CV diagram, two pairs of redox peaks were obsd. with E.ident.-0.678 V and E.ident.-0.985 V (SCE). Control expts. with apo and reconstituted SOD proteins suggested that E and E were attributed to the redox of Cu and Zn resp. From these values, **pKa** of the bridging **imidazolate** residue was calcd. to be 8.15 and the mol. area was calulated as well.

L5 ANSWER 6 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1999:290295 CAPLUS
DN 131:36377
TI C(2)-H isotopic exchange in coordinated imidazoles revisited. The case of the [Co(NH3)5ImH]3+ ion
AU Clark, Charles R.; Blackman, Allan G.; Grimmett, M. Ross; Mobinikhaledi, Akbar
CS The Department of Chemistry, University of Otago, Dunedin, N. Z.
SO Canadian Journal of Chemistry (1999), 77(2), 178-181
CODEN: CJCHAG; ISSN: 0008-4042
PB National Research Council of Canada
DT Journal
LA English
AB The temp. dependence of the acid ionization consts. of [Co(NH3)5ImH]3+ in H2O (I = 1.0 M (NaClO4)): **pKa** (.degree.C) = 10.10 0.04 (25.0), 9.92 + 0.03 (30.0), 9.82 + 0.02 (35.0), 9.62 + 0.03 (40.0), and [Co(ND3)5ImD]3+ in D2O (I = 0.35 M (NaClO4)): **pKa** (.degree.C) = 10.58 .+-. 0.06 (25.0), 9.46 .+-. 0.08 (60.0) is reported. Obsd. first-order rate consts. for H/D exchange at C-2 in [Co(ND3)5ImD]3+ over the pD range 8.08-11.20 (60.0.degree.C, I = 0.35 M (NaClO4)) follow an equation of the form: kobs = kODKw/(aD+ + Ka).gamma..+-., with kOD (0.27 .+-. 0.06 M-1 s-1) corresponding to the rate const. for OD--catalyzed abstraction of H-2 in [Co(ND3)5ImD]3+, and Ka ((2.8 .+-. 0.7) .times. 10-10 M, **pKa** = 9.55 .+-. 0.13) to the acid ionization const. of this species. No evidence was found for a pathway to H/D exchange in the **imidazolate** moiety of [Co(ND3)5Im]2+.
RE.CNT 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 7 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1996:726949 CAPLUS
DN 126:83602
TI Reactions of the cis-diamminediaquaplatinum(II) cation with histidine and related molecules
AU Appleton, Trevor G.; Ross, Fraser B.
CS Department of Chemistry, The University of Queensland, Brisbane, Qld., 4072, Australia
SO Inorganica Chimica Acta (1996), 252(1-2), 79-89
CODEN: ICHAA3; ISSN: 0020-1693
PB Elsevier
DT Journal
LA English
AB The reaction of cis-[Pt(NH3)2(H2O)2]2+ (1) with histidine (H3his+) at pH 2-3 gave initially complexes with histidine bound through carboxylate only, then, after standing, the complex contg. an amine N (NA), carboxylate O-chelate ring, [Pt(NH3)2(H2his-NA,O)]2+. Increasing the pH to 8-9 caused loss of one imidazole proton, followed by isomerization to the species with a imidazole N(3), NA-chelate ring, [Pt(NH3)2(Hhis-NA,N(3))]+. From the variation of NMR parameters with pH, **pKa** for loss of the last imidazole proton was detd. (11.2 .+-. 0.1). Histidine Me ester and histidinamide each reacted slowly with 1 at pH 5.5 to give the NA,N(3)-chelate complex. With N-(histidyl)glycine the initial complexes at pH 5 contained the ligand bound only through carboxylate, but a NA,N(3)-chelate complex then formed. With an excess of 1, a 2nd diammineplatinum moiety was bound, initially through the free carboxylate, then chelated by carboxylate and peptide N. With N-acetylhistidine and

N-(.beta.-alanyl)histidine at pH 4-5, the initial complexes also contained carboxylate-bound ligands, then a chelate ring was formed involving carboxylate and the deprotonated amide or peptide N, NA. With N-(glycyl)histidine, more complex reactions involving the terminal N atom also occurred. In alk. soln., these NA,O-chelate complexes reacted slowly to form a dinuclear complex with one ligand bound to one Pt atom through NA and N(3), and to the 2nd Pt through N(1) of bridging **imidazolate**. The 2nd ligand was bound monodentate to the 2nd Pt through NA.

L5 ANSWER 8 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1995:726567 CAPLUS
DN 123:105602
TI Origin of the pH-Dependent Spectroscopic Properties of Pentacoordinate Metmyoglobin Variants
AU Bogumil, Ralf; Maurus, Robert; Hildebrand, Dean P.; Brayer, Gary D.; Mauk, A. Grant
CS Department of Biochemistry and Molecular Biology, University of British Columbia, Vancouver, BC, V6T 1Z3, Can.
SO Biochemistry (1995), 34(33), 10483-90
CODEN: BICHAW; ISSN: 0006-2960
DT Journal
LA English
AB The pH dependence of the electronic and EPR spectra of two variants of horse heart myoglobin (Mb) in which the distal His64 ligand has been replaced by either Thr or Ile has been studied. Both of these variants exhibit spectroscopic changes with pH that are indicative of a transition between two ferric high-spin forms that occurs with a **pKa** of 9.49 for the His64Thr variant and 9.26 for the His64Ile variant and that is distinctly different from the pH-dependent spectroscopic changes related to titrn. of the distal aquo ligand of wild-type Mb. The electronic and EPR spectra of both variants at all values of pH studied are consistent with the presence of a pentacoordinate heme iron center. For the His64Thr variant, a high-resoln. (1.9 .ANG.) structure detn. establishes the lack of the distal aquo ligand and demonstrates an out-of-plane movement of the ferric iron toward the proximal histidine together with a decrease of the Fe-His bond length. Investigation of this pH-linked equil. by EPR spectroscopy reveals rhombically split high-spin signals at both pH 7 and 11 with a greater degree of rhombicity exhibited by the alk. species. The authors propose that the pH-linked spectroscopic transition exhibited by these distal histidine variants results from the deprotonation of the proximal His93 residue to produce **imidazolate** ligation at alk. pH.

L5 ANSWER 9 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1994:157441 CAPLUS
DN 120:157441
TI Heme-heme oxygenase complex. Structure of the catalytic site and its implication for oxygen activation
AU Takahashi, Satoshi; Wang, Jianling; Rousseau, Denis L.; Ishikawa, Kazunobu; Yoshida, Tadashi; Host, Janette R.; Ikeda-Saito, Masao
CS AT and T Bell Laboratories, Murray Hill, NJ, 07974, USA
SO J. Biol. Chem. (1994), 269(2), 1010-14
CODEN: JBCHA3; ISSN: 0021-9258
DT Journal
LA English
AB Heme oxygenase, a central monooxygenase enzyme of the heme catabolism and the assocd. generation of carbon monoxide, forms a 1:1 stoichiometric complex with iron protoporphyrin IX, which is a prosthetic active center and at the same time the substrate of the enzyme. By using EPR, resonance Raman, and optical absorption spectroscopic techniques, the axial ligand coordination of the enzyme-heme complex was detd. The ferric heme iron in the heme-enzyme complex at neutral pH is 6-coordinate high spin, whereas at alk. pH (**pKa** 7.6), the complex becomes low spin. Spectra of

ferrous forms of the complex indicate that histidine serves as the iron proximal axial ligand and that the residue is in its neutral imidazole rather than its **imidazolate** protonation state. Thus, the active site of the heme-heme oxygenase complex has a myoglobin-like structure rather than an active site similar to the large cytochrome P 450 class of monooxygenases. As a consequence, the activated form of the heme-heme oxygenase complex, a peroxo intermediate, is different from that of the cytochrome P 450 monooxygenases, in which the activated form is an oxo intermediate. The overall catalytic mechanism is probably more closely related to that of other monooxygenases with myoglobin-like active sites, such as secondary amine monooxygenase.

L5 ANSWER 10 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1992:545432 CAPLUS
DN 117:145432
TI Redox control of proton transfers in membrane b-type cytochromes: an absorption and resonance Raman study on bis(imidazole) and bis(**imidazolate**) model complexes of iron-protoporphyrin
AU Desbois, A.; Lutz, M.
CS Lab. Biophys., Inst. Biol. Phys. Chim., Paris, F-75005, Fr.
SO Eur. Biophys. J. (1992), 20(6), 321-35
CODEN: EBJOE8; ISSN: 0175-7571
DT Journal
LA English
AB Optical absorption spectra and resonance Raman (RR) spectra, obtained with Soret excitation, are reported for bis(imidazole) and bis(**imidazolate**) complexes of iron(II)- and iron(III)-protoporphyrin IX, prepd. aq. conditions. Perdeuteration expts. on the axial ligands permitted the assignment of the sym. Fe-(ligand)2 stretching mode of Fe[x]PP(L)2 to RR bands at 203 (x = II; L = ImH), 212 (x = II; L = Im-), 210 (x = III; L = Imh) and 226 cm-1 (x = III; Iml). These frequency differences indicate a strengthening of the axial bonds when the imidazole deprotonation occur. The larger difference obsd. for the ferric derivs. reflects the stronger .sigma.-donor capability of the Im- anion for iron(III) over iron(II). For the ferrous derivs., the frequencies of several skeletal porphyrin modes (.nu.4, .nu.10, .nu.11 and .nu.38) are downshifted by 2-10 cm-1 upon deprotonation of the ligands. This effect corresponds to an increased back-bonding from the metal atom to the porphyrin ring when the axial ligand decreases its .pi.-acid strength. Bringing further support to this interpretation, and inverse linear relationship is established between the frequencies of .nu.(Fe(II)-L2) and .nu.11. This correlation is expected to monitor the overall H-bonding state of histidine ligands of reduced cytochromes b. On the other hand, absorption measurements have characterized large **pKa** differences for the sequential imidazole ionizations of Fe[x]PP(ImH)2 in aq. cetyltrimethylammonium bromide (9.0 and 10.8 for x = III; 13.0 and 14.1 for x - II). These titrns. show that Fe(II)PP(Im-)2 and Fe(III)PP(imH()2 are good proton-acceptor and proton-donor, resp., and suggest a model by which heme, located in a favorable environment inside a cytochrome, could couple a cycle of electron transfer with a proton transfer. Based on sequence data and structural models, it is further proposed that, in several membranes cytochrome b (b, b6, b559), a pos. charged amino acid residue and an **imidazolate** ligand of the ferriheme could form an ion pair involved in a redox control of proton transfer.

L5 ANSWER 11 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1992:507283 CAPLUS
DN 117:107283
TI Temperature- and pH-dependent changes in the coordination sphere of the heme c group in the model peroxidase N.alpha.-acetyl microperoxidase-8
AU Wang, Jinn Shyan; Tsai, Ah Lim; Heldt, Janina; Palmer, Graham; Van Wart, Harold E.
CS Dep. Chem., Florida State Univ., Tallahassee, FL, 32306, USA
SO J. Biol. Chem. (1992), 267(22), 15310-18

CODEN: JBCHA3; ISSN: 0021-9258
DT Journal
LA English
AB The pH- and temp.-dependent changes in the coordination sphere of the heme c group of N.alpha.-acetyl microperoxidase-8 (Ac-MP-8) have been studied by examg. its optical, resonance Raman, ESR, and magnetic CD spectra. An optical titrn. indicates that Ac-MP-8 exists in three major ionization forms over the pH 1-12 range that are linked by **pKa** values of approx. 3 and 9. The acid form that is present at pH 1.5 exists as a mixt. of five- and six-coordinate high-spin species and most likely has water or buffer ions as axial ligand(s). On titrn. to pH 7, the His18 residue is deprotonated and becomes the proximal ligand to the iron to give a six-coordinate neutral form that has water as the sixth ligand. This form exists in a thermal high-spin intermediate-spin state equil. On raising the pH to 10, an alk. form is generated which is predominantly a five-coordinate high-spin species. It is formed by ionization of the proximal His18 residue to its **imidazolate** form with concomitant dissocn. of the water ligand at the sixth site. At concns. of Ac-MP-8 greater than 10 .mu.M, some six-coordinate low-spin species are formed that are attributed to a dimer in which a His18 residue from a second mol. of Ac-MP-8 coordinates to the sixth site of another to give a bis-His complex. Raising the pH to 11.5 does not produce an appreciable amt. of the six-coordinate complex with hydroxide as the sixth ligand. These studies show that Ac-MP-8 is a good water-sol. model for the peroxidases that exhibits minimal aggregation at concns. below 10 .mu.M in the neutral and alk. pH regions.

L5 ANSWER 12 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1992:74764 CAPLUS
DN 116:74764
TI Synthesis, properties, and complexation of a new imidazole-pendant macrocyclic 12-membered triamine ligand
AU Kimura, Eiichi; Kurogi, Yasuhisa; Shionoya, Mitsuhiko; Shiro, Motoo
CS Sch. Med., Hiroshima Univ., Hiroshima, 734, Japan
SO Inorg. Chem. (1991), 30(24), 4524-30
CODEN: INOCAJ; ISSN: 0020-1669
DT Journal
LA English
AB 2-(4-Imidazoyl)-1,5,9-triazacyclododecane (H3L) was synthesized to study its complexation behavior with ZnII and CuII, along with the ease with which the metal-bound **imidazolate** anion is generated. Zn(H3L)(ClO4)Cl shows a close equatorial coordination of the imidazole (2.025 .ANG.) in a distorted trigonal-bipyramidal structure with an addnl. Cl-. Crystal data: orthorhombic, space group Pna21, a 14.574(1), b 9.079(1), c = 13.506(1) .ANG., Z = 4, R = 0.030, Rw = 0.040. The proton dissocn. most likely from the ZnII- and CuII-coordinated imidazole occurs with **pKa** values of 10.3 and 9.3, resp., at 25.degree. and I = 0.1 (KNO3). Mixts. of [M(H3L)]3+ and [MQ]2+ and CuII (M = Cu, Zn; Q = ([12]aneN3 = 1,5,9-triazacyclododecane) in alk. MeOH soln. yield [M2(H2L)Q] bridged by the **imidazolate** anion. BL was isolated during the B2H6 redn. of 4-[4-(n-(triphenylmethyl)imidazolyl)]-1,5,9-triazacyclododecan-2-one.

L5 ANSWER 13 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1991:445021 CAPLUS
DN 115:45021
TI Neutral imidazole is the electrophile in the reaction catalyzed by triosephosphate isomerase: structural origins and catalytic implications
AU Lodi, Patricia J.; Knowles, Jeremy R.
CS Dep. Chem., Harvard Univ., Cambridge, MA, 02138, USA
SO Biochemistry (1991), 30(28), 6948-56
CODEN: BICHAW; ISSN: 0006-2960
DT Journal
LA English

AB To illuminate the role of His-95 in the catalytic reaction mediated by triosephosphate isomerase, 13C and 15N NMR titrn. studies were carried out both on the wild-type enzyme and on a mutant isomerase in which the single remaining histidine (that at the active site) isotopically enriched in the imidazole ring. 15N NMR proved esp. useful in the unambiguous demonstration that the imidazole ring of His-95 is uncharged over the entire pH range (5-9.9) of isomerase activity. The results required that the first **pKa** of His-95 was <4.5. This abnormally low **pKa** ruled out the traditional view that the pos. charged imidazolium cation of His-95 donates a proton to the developing charge on the substrate's carbonyl O atom. 15N NMR expts. on the enzyme in the presence of the reaction intermediate analog, phosphoglycolohydroxamate, showed the presence of a strong H-bond between N.epsilon.2 of His-95 and the bound inhibitor. These findings indicated that, in the catalyzed reaction, proton abstraction from C-1 of dihydroxyacetone phosphate 1st yields an enediolate intermediate that is strongly H-bonded to the neutral imidazole side-chain of His-95. The imidazole proton involved in this H-bond then protonates the enediolate, with the transient formation of the enediol-**imidazolate** ion pair. Abstraction of the OH proton on O-1 now produces the other enediolate intermediate, which collapses to give the product glyceraldehyde 3-phosphate. This initially surprising sequence is more reasonable when it is recognized that the **pKa** values of the enediol and the perturbed pKa2 of the imidazole ring of His-95 may be rather close to each other, allowing for 2 facile and rapid proton transfers that interconvert the 2 enediolates. This appears to be the 1st reported example of the participation of an **imidazolate** side-chain in an enzyme-catalyzed reaction. The imidazole ring of His-95 lies at the N-terminus of a short .alpha.-helix that will, in accord with what is known from the behavior of substituted imidazoles in soln., lower both the 1st and the 2nd **pKa** values of the side-chain of His-95.

L5 ANSWER 14 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1991:159710 CAPLUS
DN 114:159710
TI Monomeric and dimeric mixed-ligand copper(II) complexes of 2,2'-bipyridine/1,10-phenanthroline and 1-methylimidazole with imidazoles as catalysts for superoxide dismutation
AU Bhirud, R. G.; Srivastava, T. S.
CS Dep. Chem., Indian Inst. Technol., Bombay, 400 076, India
SO J. Inorg. Biochem. (1990), 40(4), 331-8
CODEN: JIBIDJ; ISSN: 0162-0134
DT Journal
LA English
AB Monomeric complexes [Cu(LL)(L')(NO3)2] (where LL is 2,2'-bipyridine or 1,10-phenanthroline and L' is 1-methylimidazole) and dimeric complexes [Cu2(LL)2(L'')]NO3 (where L'' is an anion of imidazole or 2-methylimidazole) were synthesized. These complexes showed a d-d transition in the range of 600-710 nm. The IR spectra of monomeric complexes showed that the NO3- is coordinated to Cu as a monodentate ligand through an O atom. The ESR spectra of monomeric complexes indicated that the ligands are bonded in axial environment around Cu (square pyramidal geometry) with 3 N donors occupying an equatorial plane. The ESR spectra of dimeric complexes showed a broad signal at about g = 2 with an addnl. weak signal at about g = 4. This suggested that 2 Cu atoms are in close proximity of <7 .ANG.. The ESR studies revealed that the formation of **imidazolate**-bridged binucler Cu(II) complexes from [Cu(LL)(L')(NO3)2] and imidazole was pH-dependent with apparent **pKa** values of 8.25-8.30. The superoxide dismutase activity of [Cu(phen)(L')(NO3)2], [Cu(bipy)(L')(NO3)2], and [Cu2(bipy)2(L')2(L'')]NO3 was measured and the latter 2 complexes showed better activity than the former complex.

L5 ANSWER 15 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1990:47564 CAPLUS

DN 112:47564
TI The influence of pentaamminerhodium(III) on the proton NMR spectra and pyrrole **pKas** of coordinated imidazoles and pyrazoles
AU Elliott, Michael G.; Shepherd, Rex E.
CS Dep. Chem., Univ. Pittsburgh, Pittsburgh, PA, 15260, USA
SO Transition Met. Chem. (London) (1989), 14(4), 251-7
CODEN: TMCHDN; ISSN: 0340-4285
DT Journal
LA English
AB [(NH3)5Rh(LH)]Cl3 were prepd. via the [(NH3)5Rh(O3SCF3)](O3SCF3)2 synthetic route [LH = 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, 5-methylimidazole, and pyrazole]. **PKa**'s at 25.0.degree. were detd. for [(NH3)5Rh(LH)]3+. The influence on the **pKa**'s of imidazoles is dominated by .sigma. withdrawal of the Rh(III) center and may be compensated by the presence of ring methylation by only 0.5 log units for Co(III) and Rh(III) derivs., compared to 1.3 units for the .pi.-withdrawing Ru(III) center. In the case of the .pi.-acceptor pyrazole ring, [(NH3)5Rh]3+ serves as a slight .pi.-donor and raises the **pKa** above the Co(III) analog. The 1H NMR spectra of [(NH3)5Rh(LH)]3+ exhibit a deshielding order: C-2H>C-5H>C-4H for imidazoles and: C-3H>C-5H>C-4H for pyrazole, as do their Co(III) analogs. The magnitude of .DELTA..delta. values (.DELTA..delta.-.delta.free L-.delta.complex) are virtually the same as in the Co(III) systems which shows that temp.-independent paramagnetism influences are unimportant compared to ring rehybridization in establishing chem. shifts for both the Co(III) and Rh(III) complexes. The imidazolato and pyrazolato complexes exhibit resonances upfield of the resp. substituted imidazole or pyrazole complex in keeping with more neg. charge on the rings; the influence is largest at C-2H of **imidazolates** and C-3H of pyrazolate.

L5 ANSWER 16 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1987:492465 CAPLUS
DN 107:92465
TI Hemes and hemoproteins. Part 4. Preparation, analysis, and solution chemistry of microperoxidase 9 - comparison with microperoxidase 8
AU Baldwin, David A.; Mabuya, Mavis B.; Marques, Helder M.
CS Dep. Chem., Univ. Witwatersrand, Johannesburg, 2050, S. Afr.
SO S. Afr. J. Chem. (1987), 40(2), 103-10
CODEN: SAJCDG; ISSN: 0379-4350
DT Journal
LA English
AB A simplified procedure is described for the prepn. of the heme nonapeptide, microperoxidase 9 (MP-9), in good yield and purity, by tryptic digestion of cytochrome c. MP-9 is monomeric in 50% MeOH/H2O, but dimerizes as the hydrophobic character of the solvent decreases (dissocn. const. KD = 1.22 x 104M-1 and 1.50 x 105M-1 in 20 and 0% MeOH/H2O resp.). MP-9 is sufficiently monomeric in 20% MeOH to be studied by conventional UV-visible spectroscopy. The coordination sphere of Fe(III) consists of the proximal histidine (His)-18 and H2O. The pH-dependence of the UV-visible spectrum could be accounted for by 4 reversible and concn.-independent **pKas** at 2.9, 4.45, 8.90, and 9.50. The 1st **pKa** represents very small spectroscopic changes and may involve ionization of the heme propionate groups; the 2nd is due to deprotonation of the proximal His and its coordination by Fe(III); the 3rd, by analogy with the related heme octapeptide MP-8, involves ionization of bound H2O; and the 4th arises from ionization of His-18 to form an **imidazolate** complex. Equil. consts. for binding of CN- (logK = 7.67), imidazole (logK = 4.34), and N3- (logK = 1.39) to monomeric MP-9 were detd. at 25.0.degree. in 20% MeOH-H2O. The behavior in soln. of MP-9 and MP-8 are compared.

L5 ANSWER 17 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1987:413578 CAPLUS
DN 107:13578

TI Pentaammineruthenium(II/III) imidazole and **imidazolate** complexes of 2-carboxylatoimidazolate and 2-imidazolecarboxaldehyde
AU Elliott, Michael G.; Shepherd, Rex E.
CS Dep. Chem., Univ. Pittsburgh, Pittsburgh, PA, 15260, USA
SO Inorg. Chem. (1987), 26(13), 2067-73
CODEN: INOCAJ; ISSN: 0020-1669
DT Journal
LA English
AB The (NH3)5RuL2+ and (NH3)5Ru63+ complexes of 2-substituted imidazoles, L = 2-carboxylatoimidazole (2CO2imH-) and 2-imidazolecarboxaldehyde (2CHOimH), were prepd. and characterized by UV-visible spectroscopy, potentiometric titrn. and differential-pulse voltammetry. An aldehyde carbonyl-hydrate equil. was detected for the free 2CHOimH ligand by 1H NMR and UV-visible methods. Above pH 7 the R = CHO deriv. is highly favored over the hydrate, R = CH(OH)2. Protonation at N3 of 2CHOimH induces hydration. The 2CHOimH is less hydrated than 4-formylpyridine (pfp) by .gtoreq.2 orders of magnitude while 2CHOimH2+ is more extensively hydrated than Hpfp+ by 1 order of magnitude. Coordination of either (NH3)5Ru2+ or (NH3)5Ru3+ with 2CO2imH- or 2CHOimH enhances the acidity of the pyrrole H. The effects of an org. ring substituent and the coordinated Ru center are virtually additive on stabilizing the imidazoloato form (RuIII > RuII; R = CHO > R = CO2-). The **pKa** for the complexes are given for 22.degree.. The (NH3)5RuIIL complexes exhibit 2 MLCT transitions that establish a .pi.-acceptor order for 2-substituted imidazoles with R = CHO > CO2- >> H. These MLCT bands occur at 367 and 420 nm for (NH3)5RuII(2CO2imH)+ and 467 and 583 nm for (NH3)5RuII(2CHOimH)2+. These are attributed to .pi.ring* .rarw. .pi.d and .pi.R* .rarw. .pi.d transition. The strong .pi.-acceptor character of 2CHOimH (comparable in magnitude to pyrazine) is further established by the E.degree. for (NH3)5Ru(2CHOimH)3+/2+ of 0.322 V. The LMCT bands (.pi.d .rarw. (.pi.1)L and .pi.d .rarw. (.pi.2,n)) of the (NH3)5Ru3+ complexes established the .pi.-donor order of 2-substituted imidazoles of R = CH(OH)2 > CH3 > H > CO2-. The (NH3)5RuIII(2CO2i.m.)+ dissocs. by an Id-type mechanism, .mu. = 2.0 M NaCl and 22.degree.. Substitution of 2CO2imH- on (NH3)5RuOH22+ is slower than substitution of imH: a steric rate redn. of .apprx.240 times is implicated after correction for the 10-fold rate increase for anionic vs. neutral ligands. The influence of (NH3)5Ru2+ and (NH3)5Ru3+ on 2CHOimH as a ligand is similar to their influence on pfp; RuIII strongly favors the hydration of either ligand while the substantial .pi.-acceptor character of R = CHO favors the carbonyl form. The effect is particularly strong for 2CHOimH because imidazoles are generally poor .pi.-acceptors; incorporation of R = CHO introduces the capacity of the imidazole ring to stabilize soft metal centers via a .pi.-acceptor role.

L5 ANSWER 18 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1984:502893 CAPLUS
DN 101:102893
TI Pyrazole/imidazole and pyrazolato/imidazolato complexes of pentacyanoferrate(II/III) and pentaammineruthenium(II/III). LMCT transitions of low-spin d5 complexes
AU Johnson, Craig R.; Henderson, Wayne W.; Shepherd, Rex E.
CS Dep. Chem., Univ. Pittsburgh, Pittsburgh, PA, 15260, USA
SO Inorg. Chem. (1984), 23(18), 2754-63
CODEN: INOCAJ; ISSN: 0020-1669
DT Journal
LA English
AB Ligand-to-metal charge-transfer (LMCT) bands were obsd. for the low-spin d5 complexes (CN)5FeL2- and (NH3)5RuL3+ (L = imidazole, pyrazole, (methylated imidazoles and pyrazoles, benzimidazoles, hypoxanthine, caffeine, histidines). The LMCT spectral bands appear in the visible and UV regions. The origin of the transitions may be assigned on the basis of HOMO's of imidazole and pyrazole. Deprotonation of the pyrrole NH produces the resp. imidazole or pyrazolate complex, with the LMCT spectra shifted to lower energy for aq. soln. spectra. Assignments based on

HOMO's of ligands are made for 33 imidazoles and 6 pyrazoles. The **pKa**'s of pyrazole complexes at 25.0.degree.C, .mu. = 0.10 (NaClO4), were detd. For (NH3)5RuL3+ (L = imidazole and pyrazole),the acidity of the pyrrole NH on coordination increases 5.3-fold and 8.2-fold, resp., indicative of the effect of the distance between the central Ru(III) ion and the site of deprotonation. The effect of .sigma.-withdrawal by varying the coordinated metal center and the effect of .pi.-donation by **imidazolate** or pyrazolate is discussed. The 1H NMR spectra for complexes of DL+, (NH3)5CoL3+, (CN)5CoL2-, (NH3)5RuL2+, (CN)5FeL3- (L = 3-methylpyrazole) are discussed. The effect of coordination of the following metal centers to 1-methylimidazole on the 1H NMR spectrum of the resp. complexes is reported: D+, (NH3)5Co3+, MeHg2+, (CN)5Co2-, (NH3)5Ru2+, (CN)5Fe3-. .sigma. Withdrawal overshadows other factors such as temp. independent paramagnetism in these complexes, and all resonances are shifted downfield for coordinated pyrazole, 3-methylpyrazole, and 1-methylimidazole except for (NH3)3Ru2+ and (CN)5Fe3- centers where .pi. backbonding reverses the shift of remote sites (H(5) or CH3 of 1-methylimidazole and H(4) and H(5) of pyrazole).

L5 ANSWER 19 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1984:412899 CAPLUS
DN 101:12899
TI Influence of the metal centers on the **pKa** of the pyrrole hydrogen of imidazole complexes of (NH3)53+, M(III) = Co(III), Rh(III), Ir(III), Ru(III)
AU Hoq, M. Fazlul; Shepherd, Rex E.
CS Dep. Chem., Univ. Pittsburgh, Pittsburgh, PA, 15260, USA
SO Inorg. Chem. (1984), 23(13), 1851-8
CODEN: INOCAJ; ISSN: 0020-1669
DT Journal
LA English
AB The **pKa**'s at 298 K, .mu. = 0.10 (NaCl), and the temp. dependence (273-343 K) for the deprotonation of the pyrrole NH of several imidazoles coordinated to (NH3)5M3+ moieties (M = CoIII, RhIII, IrIII, RUIII) are reported. A greater importance of dn configuration over ion size was found. 1H NMR spectra of low-spin d6 complexes of imidazoles and ring-methylated imidazoles are discussed for CoIII, RhIII, IrIII, and RuII. The C-2 and remote ring, C-5, substituents are shifted downfield relative to the free imidazole ligand in the order H+ > CoIII > RhIII > IrIII. The C-4 position is influenced competitively by .sigma.-withdrawal ring substituents and TIP effects for CoIII. Assignments of the remote isomer for (NH3)5M(2,5-Me2imH)3+ (M = CoIII, and RuIII, are made from the 1H NMR spectra of the CoIII and RuII complexes. The RuIII complex of 2,5-Me2imH and the **imidazolate** form (2,5-Me2i.m.-) both exhibit LMCT spectra. The imidazolato form has 3 bands at 655, 377, and 272 nm, proposed for .pi.1 .fwdarw. .pi.d, .pi.2 .fwdarw. .pi.d, and n .fwdarw. .pi.d transitions, where .pi.1, .pi.2, and n are the highest HOMO's of the imidazolato ring.

L5 ANSWER 20 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1983:103032 CAPLUS
DN 98:103032
TI Magnetic circular dichroism spectra of soybean leghemoglobin a at room temperature and 4.2 K
AU Sievers, Gunnel; Gadsby, Paul M. A.; Peterson, Jim; Thomson, Andrew J.
CS Sch. Chem. Sci., Univ. East Anglia, Norwich, NR4 7TJ, UK
SO Biochim. Biophys. Acta (1983), 742(3), 637-47
CODEN: BBACAQ; ISSN: 0006-3002
DT Journal
LA English
AB MCD and EPR measurements on soybean legHb a have shown that at room temp. legHb a is a mixt. of a high-spin compd. with the proximal histidine and water as the 5th and 6th ligands of heme Fe and of a low-spin deriv. which is a bishistidine compd. with proximal and distal histidines as axial

ligands. Addn. of imidazole gives a histidine-imidazole compd. with pH-dependent MCD and EPR spectra. At acid pH the compd. is similar to other bisimidazole derivs. with MCD max. at 1610 nm and EPR signals at 3.03, 2.29, and .apprx.1.50. At alk. pH the spectrum has an MCD max. at 1350 nm and g factors 2.82, 2.29, and 1.69. The spectra interconvert with a **pKa** of 6.5-7.0. At alk. pH the proton at N-1 of the exogenous imidazole is suggested to dissoc., resulting in an **imidazolate** ion bound to the Fe. LegHb can also bind PhOH. This deriv. is high-spin at room temp., but mainly low-spin at 4.2 K. The legHb-PhOH compd. may serve as a model for hemoprotein with histidine-phenolate as the 5th and 6th axial ligands.

L5 ANSWER 21 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1983:49049 CAPLUS
DN 98:49049
TI Identification of the **imidazolate** anion as a ligand in metmyoglobin by near-infrared magnetic circular dichroism spectroscopy
AU Gadsby, Paul M. A.; Thomson, Andrew J.
CS Sch. Chem. Sci., Univ. East Anglia, Norwich, NR4 7TJ, UK
SO FEBS Lett. (1982), 150(1), 59-63
CODEN: FEBLAL; ISSN: 0014-5793
DT Journal
LA English
AB The near-IR (700-1900 nm) MCD spectra of a horse heart metmyoglobin-imidazole complex have been measured as a function of pD (9.1-12.2) at room temp. Two low-spin ferric heme complexes with MCD peaks at 1600 and 1350 nm, interconvert with an apparent **pKa** of just above 11.0. Since this process is identified with the deprotonation of the added imidazole ligand at N-1, the species having its main peak at 1600 nm was identified as the histidine-imidazole complex; that at 1350 nm was identified as the histidine-**imidazolate** form. Thus, the near-IR MCD clearly discriminates between these 2 species.

L5 ANSWER 22 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1983:23051 CAPLUS
DN 98:23051
TI pH dependence of the formation of simple **imidazolate**-bridged binuclear copper(II) complexes
AU Yokoi, Hiroshi; Chikira, Makoto
CS Chem. Res. Inst. Non-Aqueous Solutions, Tohoku Univ., Sendai, 980, Japan
SO J. Chem. Soc., Chem. Commun. (1982), (19), 1125-6
CODEN: JCCCAT; ISSN: 0022-4936
DT Journal
LA English
AB ESR spectral study showed that the formation of **imidazolate** -bridged binuclear Cu(II) complexes of aminocarboxylates is pH-dependent, with a **pKa** of 8.3. This behavior parallels the one reported previously (Valentine, J. S.; et al., 1979) for zinc-free bovine erythrocyte superoxide dismutase.

L5 ANSWER 23 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1981:507657 CAPLUS
DN 95:107657
TI Synthesis, structure, and properties of an **imidazolate**-bridged copper(II)-cobalt(III) complex
AU Davis, William M.; Dewan, John C.; Lippard, Stephen J.
CS Dep. Chem., Columbia Univ., New York, NY, 10027, USA
SO Inorg. Chem. (1981), 20(9), 2928-32
CODEN: INOCAJ; ISSN: 0020-1669
DT Journal
LA English
AB [(PMDT)Cu(i.m.)Co(NH3)5](ClO4)4 (PMDT = 1,1,4,7,7-pentamethyldiethylenetriamine and Him = imidazole) was prepd. Single-crystal x-ray diffraction studies show this new, heterobimetallic

complex to crystallize in the monoclinic space group P21/c with a 15.694(4), b 15.771(4), c 14.112(3) .ANG., .beta. 112.11(2).degree., and Z = 4. The Co(III) center has five equiv. Co-NH3 bonds of 1.957(7)-1.983(5) .ANG. in length and a Co-N(**imidazolate**) bond distance of 1.933(5) .ANG.. The Cu(II) geometry is D2d distorted square planar with a Cu-N(**imidazolate**) bond of 1.954(6) .ANG. and a long axial Cu...O(perchlorate) contact of 2.856(7) .ANG.. Variable-temp. magnetic susceptibility studies of the solid complex reveal Curie-type behavior with an effective moment of 1.72 and gav = 2.07. The latter agrees with the value detd. by solid-state ESR measurements. Through a combination of pH-dependent frozen-soln. ESR, electronic spectral, and potentiometric titrn. studies, the **imidazolate** bridge was shown to split at the Cu(II) site in protic media. The **pKa** values for the mononuclear components [(NH3)5Co(imH)]3+ and [(PMDT)Cu(OH2)]2+, generated from the bridged complex in soln., are in good agreement with those reported previously.

L5 ANSWER 24 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1980:574659 CAPLUS
DN 93:174659
TI Affinities of **imidazolate** and imidazole ligands for pentacyanoiron(III)
AU Johnson, Craig R.; Shepherd, Rex E.; Marr, Bonnie; O'Donnell, Stephen; Dressick, Walter
CS Dep. Chem., Univ. Pittsburgh, Pittsburgh, PA, 15260, USA
SO J. Am. Chem. Soc. (1980), 102(20), 6227-35
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA English
AB Assocn. consts. for the reaction (CN)5Fe(H2O)2- + Ln .dblharw. (CN)5FeLn-2 + H2O were measured in .mu. = 1.00 NaCl for Ln = imidazole (Him), **imidazolate** (i.m.-), and 1-methylimidazole (1-Me-i.m.). The thermodn. parameters are (L, Kf(298 K), .DELTA.H0, .DELTA.S0): (Him, 3.4 .times. 105 M-1, -15.8 .+-. 0.6 kcal/mol, -27 .+-. 2 eu); (1-Me-i.m., 3.0 .times. 105 M-1, -13.1 .+-. 0.2 kcal/mol, -18.8 .+-. 0.5 eu); (i.m.-, 8.8 .times. 108 M-1, -25.4 .+-. 2.3 kcal/mol, -45 .+-. 8 eu). The affinity of i.m.- for (CN)5Fe2- exceeds that of CN- (Kf = 5 .times. 108); the origin of ligand affinity order toward (CN)5Fe2- is discussed. Comparisons are made for the affinities of **imidazolate** vs. imidazole as a ligand for the transition-metal complexes of series I: (CN)5Fe2-, ferrimyoglobin, cobalamin, MeHg+, and (NH3)5Ru3+. **Imidazolate** serves as a better .sigma. donor than imidazole by .apprx. 7 kcal/mol toward transition-metal complexes compared to 10 kcal toward H+. The **pKa** of the pyrrole H of imidazole in (CN)5Fe(Him)2- was studied as a function of temp.: **pKa**(299 K) = 10.93 .+-. 0.03, .DELTA.H0 = 8.8 .+-. 0.8 kcal/mol, .DELTA.S0 = -21 .+-. 3 eu (.mu. = 1.00). The results are compared to **pKa**'s for series I. The effects of imidazole ring substituents at C-5 on the **pKa** of (CN)5Fe(RimH)n-2 complexes were studied in .mu. = 1.0 NaCl (R, **pKa**): H, 10.4; CH3, 10.4; CH2CH2CO2-, 10.5; CHCHCO2-, 8.6; CH2CH2NH3+, 9.2; CH2CH(CO2-)NH3+, .apprx. 9.7. The dissocn. of the **imidazolate** ligand from (CN)5Fe(i.m.)3- occurs with parallel solvent-assisted and proton-assisted pathways. Activation parameters for the k0 pathway are given. Formation of the **imidazolate** complex from (CN)5FeOH3- and Him occurs by a 1st-order path in [Him] with kf(298 K) = 0.141 .+-. 0.009 M-1 s-1, .DELTA.H.thermod. = 20.2 .+-. 2.0 kcal-. The mechanism for dissocn. of i.m.- from (CN)5Fe(i.m.)3- and formation of (CN)5Fe(i.m.)3- from (CN)5FeOH3- and Him are discussed in terms of an Id mechanism.

L5 ANSWER 25 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1979:588678 CAPLUS
DN 91:188678
TI pH-dependent migration of copper(II) to the vacant zinc-binding site of zinc-free bovine erythrocyte superoxide dismutase

AU Valentine, Joan S.; Pantoliano, Michael W.; McDonnell, Peter J.; Burger, Allan R.; Lippard, Stephen J.
CS Dep. Chem., Rutgers, State Univ., New Brunswick, NJ, 08903, USA
SO Proc. Natl. Acad. Sci. U. S. A. (1979), 76(9), 4245-9
CODEN: PNASA6; ISSN: 0027-8424
DT Journal
LA English
AB Bovine erythrocyte superoxide dismutase (Cu2Zn2SODase) (EC 1.15.1.1) consists of 2 identical subunits each contg. Cu2+ and Zn2+ in close proximity. ESR and visible absorption spectroscopic studies of the zinc-free deriv. of this protein, Cu2E2SODase (E = empty) over the pH range 6-10 are described. The ESR spectrum of the zinc-free protein at 77 K is markedly pH dependent. At pH <8.0, the ESR spectrum is axial in appearance. At pH >8.0, the lineshape becomes increasingly distorted with increasing pH until, at pH 9.5, the spectrum is very broad and resembles that of the 4-copper deriv., Cu2Cu2SODase and of model **imidazolate** -bridged binuclear Cu(II) complexes. ESR spectra at 30.degree. are also consistent with formation of Cu(II)-Im-Cu(II). A plot of changes in the signal amplitude of g.perp. for Cu2E2SODase as a function of pH gives an apparent **pKa** of 8.2 for the transition. The long-wavelength absorption with .lambda.max = 700 nm characteristic of Cu2E2SODase shifts with increasing pH to 800 nm and the resulting visible spectrum is identical to that of Cu2Cu2SODase. All of the above-mentioned spectroscopic changes induced by addns. of NaOH are reversed when the pH is decreased with HNO3, although the approach to equil. is slow in the latter case. The results of these expts. are consistent with a reversible, pH-dependent migration of Cu2+ from the native copper site of one subunit of the zinc-free protein to the empty zinc site of another subunit. By contrast, native protein, Cu2Zn2SODase, and the 4-copper protein, Cu2Cu2SODase, show no variation in visible or ESR spectral properties in this pH range. Some previous results concerning the activity of Cu2E2SODase and its thermal stability are reexamd. in light of these new findings.

L5 ANSWER 26 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1977:1656 CAPLUS
DN 86:1656
TI Reactivity of coordinated nucleophiles. A comparison of metal bound **imidazolate** and hydro xide ions as models for carbonic anhydrase
AU Harrowfield, J. M.; Norris, V.; Sargeson, A. M.
CS Res. Sch. Chem., Aust. Natl. Univ., Canberra, Aust.
SO J. Am. Chem. Soc. (1976), 98(23), 7282-9
CODEN: JACSAT
DT Journal
LA English
AB The cleavage of 4-nitrophenyl acetate by the simple metal complexes (NH3)5CoOH2+ and (NH3)5CoIm2+ (Im = N-deprotonated imidazole) was studied in H2O andMe2SO solvents. In both solvents for both complexes the reactions are exclusively nucleophilic, as demonstrated by the detection of the acetylated reactants, (NH3)5CoO2CCH32+ and (NH3)5CoImCOCH33+. The **pKa** detd. titrimetrically for (NH3)5CoImH3+ in water (25.degree., .mu. = 1.0, NaClO4) is 10.0 and the large difference in nucleophilic capacity towards 4-nitrophenyl acetate between (NH3)5CoIm2+ (kN = 9M-1s-1, 25.degree., .mu. = 1.0, NaClO4) and (NH3)5CoCH2+ (kN = 1.5 .times. 10-3M-1sec-1) is closely parallel to the difference in basicity (**pKa** (NH3)5CoOH23+ = 6.4, 25.degree., .mu. = 1.0, NaClO4). In Me2SO the complexes are of similar activity towards the ester (kIm = 30M-1sec-1, kOH = 0.72M-1sec-1, 25.degree.) and this may be largely attributed to a marked increase in the basicity of (NH3)5CoOH2+ relative to that of (NH3)5CoIm2+ in this dipolar, aprotic solvent. Similar trends for DMF are indicated and mechanistic and kinetic aspects of this study are discussed in relation to the esterase properties of the zinc metalloenzyme, carbonic anhydrase.

L5 ANSWER 27 OF 27 CAPLUS COPYRIGHT 2002 ACS
AN 1975:166708 CAPLUS
DN 82:166708
TI Magnetic resonance study of exchangeable protons in human carbonic anhydrases
AU Gupta, Raj K.; Pesando, John M.
CS Fox Chase Cancer Cent., Inst. Cancer Res., Philadelphia, Pa., USA
SO J. Biol. Chem. (1975), 250(7), 2630-4
CODEN: JBCHA3
DT Journal
LA English
AB A titratable exchangeable proton resonance assignable to a histidine imidazole ring N-H proton was obsd. .apprx.-15 ppm downfield from tetramethylsilane. The chem. shift of this resonance was affected by sulfonamide and anion inhibitors and by removal of Zn or replacement of Zn by Co, indicating that the proton is located at or near the active site. The pH dependence of the chem. shift of this resonance, which was abolished by inhibitors, reflected the titration of a group with a **pKa** of 7.3 in human carbonic anhydrase B and .ltoreq. 7.1 in human carbonic anhydrase C. These **pKa** values are interpreted as due to the ionization of a neutral imidazole to form the **imidazolate** anion coordinated to Zn. A mechanism for enzymic catalysis involving reversible deprotonation and coordination of a histidine to the metal is consistent with these studies.

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=> s imidazolate
           504 IMIDAZOLATE
            28 IMIDAZOLATES
L8          511 IMIDAZOLATE
                (IMIDAZOLATE OR IMIDAZOLATES)

=> s l8 and sodium
        753630 SODIUM
            31 SODIUMS
        753643 SODIUM
                (SODIUM OR SODIUMS)
L9          31 L8 AND SODIUM

=> s l9 and depolymerization
          6441 DEPOLYMERIZATION
            27 DEPOLYMERIZATIONS
          6453 DEPOLYMERIZATION
                (DEPOLYMERIZATION OR DEPOLYMERIZATIONS)
          9313 DEPOLYMN
            36 DEPOLYMNS
          9325 DEPOLYMN
                (DEPOLYMN OR DEPOLYMNS)
         12548 DEPOLYMERIZATION
                (DEPOLYMERIZATION OR DEPOLYMN)
L10          1 L9 AND DEPOLYMERIZATION

=> s l9 and elimination
        132659 ELIMINATION
          1568 ELIMINATIONS
        133157 ELIMINATION
                (ELIMINATION OR ELIMINATIONS)
L11          0 L9 AND ELIMINATION

=> s l8 and elimination
        132659 ELIMINATION
          1568 ELIMINATIONS
        133157 ELIMINATION
                (ELIMINATION OR ELIMINATIONS)
L12          4 L8 AND ELIMINATION

=> dis l12 1-4 ibib abs

L12  ANSWER 1 OF 4  CAPLUS  COPYRIGHT 2002 ACS
ACCESSION NUMBER:         1995:647330  CAPLUS
DOCUMENT NUMBER:          123:159256
TITLE:                    Binding of the {MoFe3S4}3+ core by a tridentate
                          thiolate and chemical analogs of the molybdenum
                          coordination environment in the iron-molybdenum
                          cofactor of nitrogenase
AUTHOR(S):                Barclay, J. Elaine; Evans, David J.; Garcia, Gabriel;
                          Santana, M. Dolores; Torralba, M. Carmen; Yago, Juan
                          M.
CORPORATE SOURCE:         John Innes Centre, Univ. Sussex, Brighton, BN1 9RQ, UK
SOURCE:                   J. Chem. Soc., Dalton Trans. (1995), (12), 1965-71
                          CODEN: JCDTBI; ISSN: 0300-9246
DOCUMENT TYPE:            Journal
LANGUAGE:                 English
AB   The tridentate thiol 1,4,7-tris(4-sulfanylbenzoyl)-1,4,7-triazacyclononane
     (H3L) on deprotonation ligated to each of the Mo-Fe-S clusters
     [NEt4][MoFe3S4(SEt)4(dmpe)] (1) [dmpe = 1,2-bis(dimethylphosphino)ethane]
     and [NEt4]2[MoFe3S4(SEt)3(tccat)(solv)] [H2tccat = 3,4,5,6-
     tetrachlorocatechol; solv = DMSO or MeCN], with elimination of
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ethanethiol, to give [NEt4][MoFe3S4L(SEt)(dmpe)] (2) and [NEt4]2[MoFe3S4L(tccat)(solv)] (solv = DMSO 4 or MeCN 5) resp. Cluster 2 reacted with 1 equiv of trimethylacetyl chloride to give [NEt4][MoFe3S4L(Cl)(dmpe)] (3). The clusters 2-5 were characterized by 1H NMR, IR and Moessbauer spectroscopies and by elemental microanalyses. Reaction of 4 with imidazole, Et4N+ **imidazolate**, or the Et4N+ salt of histidine Me ester generated clusters, isolated as black solids, in which the Mo coordination environment, NO2S3, is similar to that of Mo in the Fe-Mo cofactor of nitrogenase. Similar reactions were obsd. for the related cluster [NEt4]2[MoFe3S4(SEt)3(tccat)(solv)]. 1H NMR, IR and Moessbauer parameters are reported.

L12 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2002 ACS
ACCESSION NUMBER: 1995:199032 CAPLUS
DOCUMENT NUMBER: 122:44933
TITLE: Thermal latent coordination compounds. The thermal degradation of imidazole and pyrazole adducts of metal acetates
AUTHOR(S): Doering, M.; Ludwig, W.; Goerls, H.
CORPORATE SOURCE: Inst. Inorganic Analytical Chem., Univ. Jena, Jena, Germany
SOURCE: Journal of Thermal Analysis (1994), 42(2-3), 443-59
CODEN: JTHEA9; ISSN: 0368-4466
PUBLISHER: Akademiai Kiado
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The thermal behavior of complexes M(HIm)2(OAc)2 (HIm = imidazole, M = Co, Ni, Cu) is different. Similar to the thermal degrdn. of Ni(acac)2(HIm)2, the Ni(HIm)2(OAc)2 loses acetic acid to form Ni(Im)2. All nitrogen ligands are split off from the copper complex by formation of stable basic copper acetate. The cobalt compd. eliminated acetic acid partially while acetate and **imidazolate** bridging species are obtained. The thermal behavior of the acetate complexes of pyrazole and the bulky 3,5-dimethylpyrazole is quite similar. In a 1st step pyrazolium acetate is removed. The crystal structure of Ni(HPz)4(OAc)2 (HPz = pyrazole) is detd. by x-ray diffraction: monoclinic, space group C2/c. The water mol. represents the center of two N-H...O-H...O-bridges. The system of H-bridges in the compd. relieves the proton transfer, indicated by the **elimination** of pyrazolium acetate.

L12 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2002 ACS
ACCESSION NUMBER: 1987:176860 CAPLUS
DOCUMENT NUMBER: 106:176860
TITLE: Synthesis of oligophosphopeptides and related ATP .gamma.-peptide esters as probes for cAMP-dependent protein kinase
AUTHOR(S): Johnson, Thomas B.; Coward, James K.
CORPORATE SOURCE: Dep. Chem., Rensselaer Polytech. Inst., Troy, NY, 12180-3590, USA
SOURCE: J. Org. Chem. (1987), 52(9), 1771-9
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 106:176860
AB Hexapeptides Ac-Leu-Arg-Arg-Ala-Ser(R)-Leu-Gly-R1 (I; R = H; R1 = OMe, NHMe) and the corresponding phosphopeptides I [R = P(O)(OH)2] were prepd. by conventional soln. methods. The phosphopeptides were obtained by phosphorylation with (PhO)2P(O)Cl. I (R = H) were substrates for cAMP-dependent protein kinase. ATP .gamma.-peptide esters Ac-X-Ala-Ser(ATP)-X1-OMe (X = null, X1 = Leu; X = Arg, Leu, X1 = null) were prepd. via condensation of phosphopeptides with ADP **imidazolate**.

L12 ANSWER 4 OF 4 CAPLUS COPYRIGHT 2002 ACS

ACCESSION NUMBER: 1979:490783 CAPLUS
DOCUMENT NUMBER: 91:90783
TITLE: Fluorine reactivity in 2-(trifluoromethyl)imidazoles
AUTHOR(S): Kimoto, Hiroshi; Cohen, Louis A.
CORPORATE SOURCE: Natl. Inst. Arthritis, Metab. Dig. Dis., NIH, Bethesda, MD, 20014, USA
SOURCE: J. Org. Chem. (1979), 44(16), 2902-6
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
AB 2-(Trifluoromethyl)imidazole undergoes facile alk. hydrolysis to imidazole-2-carboxylic acid, the 4-Me deriv. being 12-fold as reactive as the parent compd. The rate-limiting step is the solvent-assisted internal **elimination** of F-from the **imidazolate** anion to give a transient difluorodiazafulvene. Formation of the carboxylic acid is retarded by added F-, demonstrating the reversibility of the **elimination** step. Alcoholysis to orthoesters involves the same difluorodiazafulvene intermediate but is 200-fold slower than hydrolysis because of the weaker solvating power of alcs. In alk. media, the tri-Et orthoester loses a mol. of alc. to form the moderately stable diethoxydiazafulvene. Protonation of the imidazole ring retards acid hydrolysis of the orthoesters 60-fold relative to trialkyl orthobenzoates. 2-(Trifluoromethyl)imidazoles are converted directly to 2-cyanoimidazoles (90% yield) in aq. NH3; as in hydrolysis and alcoholysis, formation of the difluorodiazafulvene is rate limiting. The value of kobsd for cyanoimidazole formation increases with the water content for the ammonia soln. The reactivity of the trifluoromethyl group is lost following N-alkylation of the imidazole ring.